

MULTIPLE SPECTRA<sup>1</sup>

## III.

I HAVE endeavoured to show in the previous articles that there are many facts which justify the conclusion that the same elementary substance in a state of purity can under different conditions give us spectra different in kind. To those spectra to which special reference is now made the names of *lined* and *fluted* have been given to mark their chief point of difference, which is that in lined spectra we deal with lines distributed irregularly over the spectrum; while in fluted spectra we deal with rhythmical systems.

This was the first point, and I showed that the idea was suggested that the lined and fluted spectra, though produced by the same substance, were produced by that substance in a different molecular condition.

I have pointed out that both in lined and fluted spectra taken separately there was evidence of still further complication, that is, that a complete lined spectrum of a substance and a complete fluted spectrum of a substance, was the result of the vibration not of one kind of molecule only, but probably of several.

So that in this view we have to imagine a series, in some cases a long series, of molecular simplifications brought about by the action of heat, and ascribe the spectral changes to these simplifications.

To understand my contention, and one objection which has been taken to it, in the clearest way, let us suppose that there is a substance which gives us, under different conditions, three spectra, which we will term *a*, *b*, and *c*. My view is that these spectra are produced by three distinct molecular groupings brought about by successive dissociations. On the other hand, it is objected that they are produced by *one and the same molecule* struck, as a bell might be struck, *in different ways* by the heat waves or the electric current passing among the molecules.

In my memoir entitled "Discussion of the Working Hypothesis that the so-called Elements are Compound Bodies," I remarked as follows:—

"I was careful at the very commencement of this paper to point out that the conclusions I have advanced are based upon the analogies furnished by those bodies which, by common consent and beyond cavil and discussion, are compound bodies. Indeed, had I not been careful to urge this point, the remark might have been made that the various changes in the spectra to which I shall draw attention are not the results of successive dissociations, but are effects due to putting the same mass into different kinds of vibration or of producing the vibration in different ways. Thus the many high notes, both true and false, which can be produced out of a bell with or without its fundamental one, might have been put forward as analogous with those spectral lines which are produced at different degrees of temperature with or without the line, due to each substance when vibrating visibly with the lowest temperature. To this argument, however, if it were brought forward, the reply would be that it proves too much. If it demonstrates that the *h* hydrogen line in the sun is produced by the same molecular grouping of hydrogen as that which gives us two green lines only when the weakest possible spark is taken in hydrogen inclosed in a large glass globe, it also proves that calcium is identical with its salts. For we can get the spectrum of any of the salts alone without its common base, calcium, as we can get the green lines of hydrogen without the red one.

"I submit, therefore, that the argument founded on the over-notes of a sounding body, such as a bell, cannot be urged by any one who believes in the existence of any compound bodies at all, because there is no spectroscopic break between acknowledged compounds and the supposed elementary bodies. The spectroscopic differences

between calcium itself at different temperatures is, as I shall show, as great as when we pass from known compounds of calcium to calcium itself. There is a perfect continuity of phenomena from one end of the scale of temperature to the other."

Not only is what may be termed the bell hypothesis opposed to the law of continuity, as I endeavoured to show in the last paragraphs quoted, but it appears never to have struck the objectors that it is also opposed to the theory of exchanges as it is generally enunciated, on which the whole of our supposed knowledge of extra-terrestrial matter depends. If vapours, when relatively cool, do not absorb the same wave-lengths which they give out when relatively hot, what becomes of some of the most noted exploits of our nineteenth-century science?

Take the case of sodium. Three distinct spectra have been mapped for it. There is first the yellow line seen in a Bunsen flame, then the green line seen alone in a vacuum tube when the vapour is illuminated by an electric glow, and again there is the fluted absorption spectrum, without any lines, seen when sodium is gently heated in hydrogen in a glass tube. If we have here the same molecule agitated in different ways, I ask which is the true spectrum of sodium? And what right have we to say that sodium exists in the sun because the yellow line is represented? Why do we not rather say that sodium does *not* exist in the sun because the fluted spectrum is *not* represented.

It is not necessary to enlarge upon this point because the difficulty in which the theory of exchanges is thus landed is obvious, while, if we acknowledge different molecular groupings in the vapours of the same chemical substance, and apply the theory of exchanges to *each grouping*, then the teachings of that theory become more numerous and important than before.

It is of course of the highest importance to see whether there is any *experimentum crucis*—any mode of inquiry—by which the theory can be settled one way or the other.

I submit that the results of experiments based on the following considerations ought to be accepted as throwing light on the question.

1. At different temperatures the brilliancy of the spectral lines of the same substances as ordinarily observed changes enormously. See if these changes can be produced *at the same temperature* by employing those experimental conditions which will be most likely to bring about different molecular conditions if such exist.

2. At a low temperature some substances give us few lines while at a high one they give us many. Vapours, therefore, already glowing with few lines at a low temperature, say in a flame, should give us all their lines when the vapour is suddenly subjected to a high one, say by the passage of a high tension spark. On the bell hypothesis the spectrum should change with the mode of striking. On the dissociation hypothesis this should only happen for the lines of those molecular groupings which are *from other considerations* held to be more simple. If the flame has brought the substance to its lowest state, the passage of the most powerful spark should not cause the flame spectrum to vary.

Now what are the "other considerations" above referred to? This necessitates a slight digression.

In the *Phil. Trans.* for 1873<sup>1</sup> I gave an historical account, showing how, when a light source such as a spark or an electric arc is made to throw its image on the slit of a spectroscope, the lines had been seen of different lengths, and I also showed by means of photographs how very definite these phenomena were. It was afterwards demonstrated that for equal temperatures chemical combination or mechanical mixture gradually reduced the

<sup>1</sup> Continued from p. 312.

<sup>1</sup> *Phil. Trans.*, 1873, p. 254.

spectrum by subtracting the shortest lines, and leaving only the long ones.

On the hypothesis that the elements were truly elementary, the explanation generally given and accepted was that the short lines were produced by a more complex vibration imparted to the "atom" in the region of greatest electrical excitement, and that these vibrations were obliterated, or prevented from arising, by cooling or admixture with dissimilar "atoms."

Subsequent work, however, has shown that of these short lines *some* are common to two or more spectra. These lines I have called basic. Among the short lines, then, we have some which are basic, and some which are not.

The different behaviour of these basic lines seemed, therefore, to suggest that *not all of the short lines of spectra were, in reality, true products of high temperature.*

That some would be thus produced and would therefore be common to two or more spectra we could understand by appealing to Newton's rule: "*Causas rerum naturalium non plures admitti debere quam quæ et veræ sint et earum phænomenis explicandis sufficient,*" and imagining a higher dissociation. It became, however, necessary to see if the others would also be accounted for.

Now if not all but only *some* of the short lines are products of high temperature, we are bound to think that the *others* are remnants of the spectra of those molecular groupings first to disappear on the application of heat.

At any particular heat-level, then, some of the short lines may be due to the vibrations of molecular groupings produced with difficulty by the temperature employed, while others may represent the fading out of the vibrations of other molecular groupings produced on the first application of the heat.

In the line of reasoning which I advanced a year ago,<sup>2</sup> both these results are anticipated, and are easily explained. Slightly varying Fig. 2 of that paper, we may imagine furnace A to represent the temperature of the jar spark, B that of the Bunsen burner, and C a temperature lower than that of the Bunsen burner (Fig. 1).

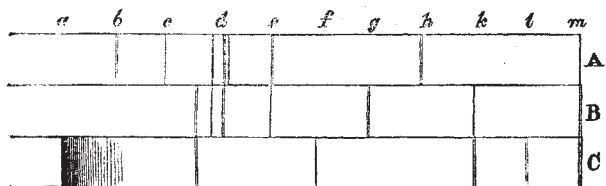


FIG. 1.—A. Highest temperature. C. Lowest temperature.

Then in the light of the paper the lines *b* and *c* would be truly produced by the action of the highest temperature, *c* would be short and might be basic, while of the lines *h* and *m*, *m* would be short and could not be basic, because it is a remnant of the spectrum of a lower temperature.

So much then by way of explanation; it is clear that to make this reasoning valid we must show that the spark, or better still the arc, provides us with a summation of the spectra of various molecular groupings into which the *solid metal which we use as poles* is successively broken up by the action of heat.

We are not limited to solid metals; we may use their salts. In this case it is shown in the paper before referred to<sup>3</sup> that in very many cases the spectrum is one much less rich in lines.

The experimental work has followed two distinct lines. I shall refer somewhat in detail to the results obtained along each. The first relates to the extraordinary and beautiful phenomena and changes observed in the spectra

of vapours of the elementary bodies when volatilised at different temperatures in vacuum tubes. Many of the lines thus seen alone and of surpassing brilliancy, are those seen as short and faint in ordinary methods of observation, and the circumstances under which they are seen suggest, if we again apply Newton's rule, that many of them are produced by complex molecules.

In this case the appeal lies to the phenomena produced when organic bodies are distilled at varying temperatures; the simplest bodies in homologous series are those volatilised at the lowest temperatures; so that on subjecting a mixture of two or more liquids to distillation, at the beginning a large proportion of the more volatile body comes over, and so on.

The novelty of the method consists in the use of the luminous electric current as an explorer and not as an agent for the supply of the vapours under examination; that is to say, the vapours are first produced by an external source of heat, and are then rendered luminous by the passage of the current. The length and bore of the tube therefore control the phenomena to a certain extent.

A form of apparatus which I have found to answer very well is shown in the accompanying woodcut (Fig. 2).

A is the tube or retort containing the metal experimented on in its lower extremity, and having a platinum wire sealed into it at a distance of about two inches from the lower end, the other end being drawn out and connected by a mercury joint to an ordinary Geissler tube, which is connected by another mercury joint to the Sprengel pump C.

Another form of tube which I have used is prepared by inserting two platinum poles into a piece of combustion tubing sealed at one end, and after inserting the metal to be experimented on, drawing out the glass between the platins to a capillary tube.

I have also tried inserting the platinum pole at the end of the retort, so that the spark passes from the surface of the metal, but this arrangement did not answer at all.

Some other modifications have been tried, but the first form I have described is that which I have found to answer best, so far as the trials have yet gone.

D is the spectroscope.

E is the lens used for focussing the image of the Geissler tube on the slit.

F is the spirit lamp for heating the retort.

H is the battery.

K and L are the wires connected with the coil.

In the second cut (Fig. 3) the method of observing the spectrum of the vapours close to the surface of the metal is indicated; the same letters apply, D' being, however, in this case a direct-vision spectroscope, which was sometimes employed for convenience.

For determining the exact positions of the lines in the spectrum of the vapour in any part of the retort, a larger spectroscope, with its illuminated scale, was used in the place of the direct-vision spectroscope.

The secondary wires of the coil were connected, one with the pole in the upper bulb at B, and the other with the platinum at A.

B is an ordinary Geissler tube with two bulbs separated by a capillary tube. The great advantage of this arrangement is that this capillary portion can be used for ascertaining what gases or vapours are carried over by the pump without any interference with the retort, both wires being connected with the Geissler tube. If, for example, we are working with sodium which contains an impurity of hydrocarbon, the moment at which it begins or ceases to come off can be found by examining the spectrum of this capillary tube.

I now give an account of the phenomena observed when we were working with sodium, in order to show the kind of phenomena and the changes observed.

After a vacuum has been obtained the retort is heated gradually. The pump almost immediately stops clicking,

<sup>1</sup> *Proc. R.S.*, vol. xxviii. p. 159.

<sup>2</sup> *Proc. R.S.*, vol. xxviii. p. 162.

<sup>3</sup> *Phil. Trans.*, 1873, p. 258.



and in a short time becomes nearly full of hydrogen. The spectrum of the capillary then shows the hydrogen lines intensely bright. After some time the gas comes off far less freely, and an approach to a vacuum is again obtained. Another phenomenon now begins to show itself: on passing the current a yellow glow is seen, which gradually fills the whole space between the pole in the retort and the metal; its spectrum consists of the lines of hydrogen and the yellow line of sodium, the red and green line being both absent until the experiment has gone on for some time.

As the distillation goes on, the yellow glow increases in brilliancy, and extends to a greater distance above the pole, and the red and green lines presently make their appearance as very faint lines.

The upper boundary of the yellow is quite sharp, the lines and fluted spectrum of hydrogen appearing above it.

After the yellow glow-giving vapour (which does not attack the glass) has been visible for some time, the pump is stopped and the metal heated more strongly. On passing the current a little while afterwards, a very

brilliant leaf-green vapour is seen underlying the yellow one, and connected with it by a sap-green vapour. The spectra then visible in the tube at the same time are—

Leaf-green	...	Green and red lines of sodium and C of hydrogen; D absent.
Sap-green	...	Green, red, and yellow sodium lines of equal brilliancy and C of hydrogen.
Yellow	...	D alone and C.
Bluish-green	...	C and F and hydrogen structure.

To observe the green sodium line alone it is necessary to point the direct-vision spectroscopie just above the surface of the metal where the green is strongest. It is also necessary to guard against internal reflections from the glass, as this may sometimes cause the D line to be seen by reflection from the surface.

This method of inquiry has been tried also with potassium, calcium, and some other metals, and with metallic salts.

With potassium and calcium we get the same inversion of phenomena, the yellow-green lines of potassium being

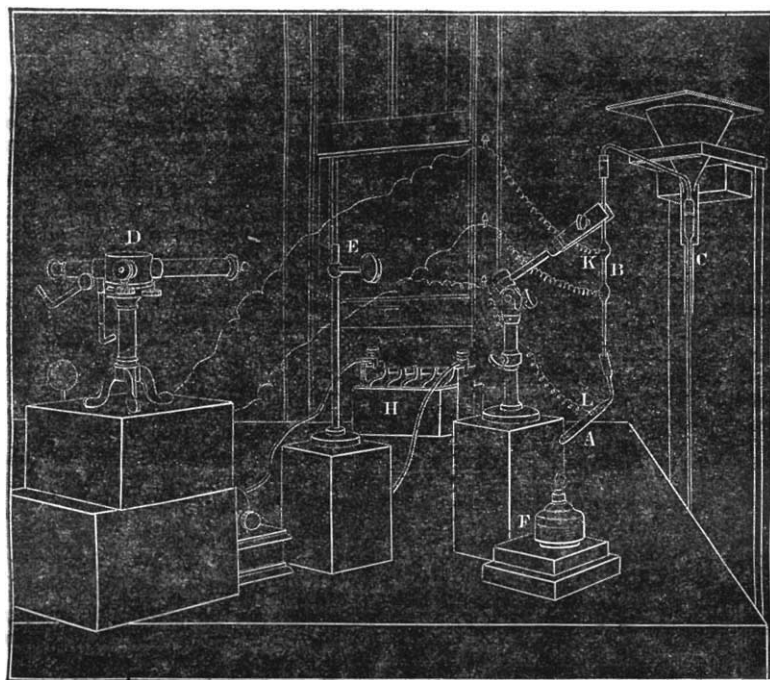


FIG. 2.—Distillation Apparatus.

seen without the red; while in the case of calcium the blue line alone was seen.

The fact that in these experiments we get, as before mentioned, vapours which at one and the same time exhibit different colours and different spectra at different levels in the tube, at once suggests the phenomena of fractional distillation.

It is also suggested, as a result of the application of this new method, that in the case of a considerable number of chemical substances not only the line spectrum is compound in its origin, as I suggested many years ago, but that a large number of the lines is due to molecular groupings of considerable complexity, which can be kept out of the reaction by careful low temperature distillation.

So much then for one method. Now for the other.

In this I have attempted to gain new evidence in the required direction by adopting a method of work with a spark and a Bunsen flame, which Col. Donnelly suggested I should use with a spark and an electric arc. This con-

sists in volatilising those substances which give us flame spectra in a Bunsen flame and passing a strong spark through the flame, first during the process of volatilisation, and then after the temperature of the flame has produced all the simplification it is capable of producing.

The results have been very striking; the puzzles which a comparison of flame spectra and the Fraunhofer lines has set us find, I think, a solution; while the genesis of spectra is made much more clear.<sup>1</sup>

To take an instance, the flame spectrum of sodium gives us, as its brightest, a yellow line, which is also of marked importance in the solar spectrum. The flame spectra of lithium and potassium give us, as their brightest, lines in the red which have not any representatives among the Fraunhofer lines, although other lines seen with higher temperatures are present.

Whence arises this marked difference of behaviour?

<sup>1</sup> I allude more especially to the production of triplets, their change into quartets, and in all probability into flutings, and to the vanishing of flutings into lines, by increasing the rate of dissociation.

From the similarity of the flame spectrum to that of the sun in one case, and from the dissimilarity in the other, we may imagine that in the former case—that of sodium—we are dealing with a body easily broken up, while lithium and potassium are more resistant; in other words, in the case of sodium, and dealing only with lines recognised generally as sodium lines, the flame has done the work of dissociation as completely as the sun itself. Now it is easy to test this point by the method now under consideration, for if this be so then (1) the chief lines and flutings of sodium should be seen in the flame itself, and (2) the spark should pass through the vapour after complete

volatilisation has been effected without any visible effect.

Observation and experiment have largely confirmed these predictions. Using two prisms of  $60^\circ$  and a high-power eyepiece to enfeeble the continuous spectrum of the densest vapour produced at a high temperature, the green lines, the flutings recorded by Roscoe and Schuster, and another coarser system of flutings, so far as I know not yet described, are beautifully seen. I say largely, and not completely, because the double red line and the lines in the blue have not yet been seen in the flame, either with one, two, or four prisms of  $60^\circ$ , though

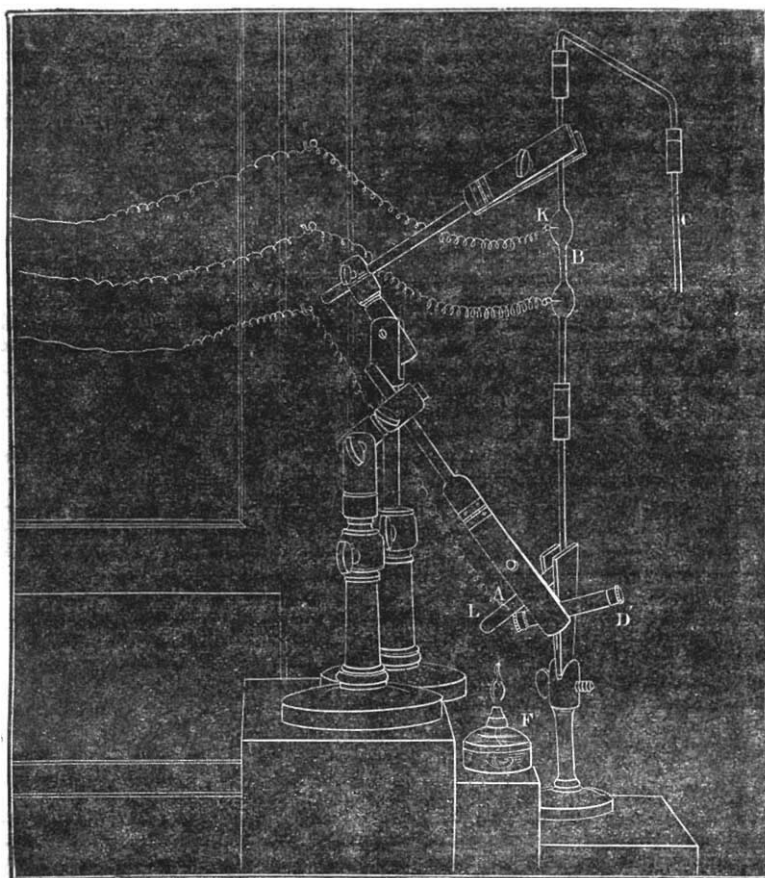


FIG. 3.—Position of Spectroscope for discovering Vapours close to the Metal.

the lines are seen *during volatilisation* if a spark be passed through the flame. Subsequent inquiry may perhaps show that this is due to the sharp boundary of the heated region, and to the fact that the lines in question represent the vibrations of molecular groupings more complex than those which give us the yellow and green lines. The visibility of the green lines, *which are short*, in the flame, taken in connection with the fact that they have been seen alone in a vacuum tube, is enough for my present purpose.

With regard to the second point, the passage from the heat-level of the flame to that of the spark *after* volatilisation is complete, produces no visible effect, indicating that in all probability the effects heretofore ascribed to *quantity* have been due to the presence of the molecular groupings of greater complexity. *The more there is to dissociate, the more time is required to run through the series, and the better the first stages are seen.*

J. NORMAN LOCKYER

(To be continued.)

WILLIAM LASSELL, LL.D., F.R.S.<sup>1</sup>

THE scientific world will receive with deep regret the intelligence of the death of this distinguished astronomer. The smaller circle of those who knew Mr. Lassell personally will deplore the loss of a friend of rare worth. Mr. Lassell passed away without suffering soon after five

o'clock on the morning of Tuesday, October 5, in the eighty-second year of his age, full of years and greatly honoured and respected.

In the words of Sir John Herschel, Mr. Lassell "belonged to that class of observers who have created their own instrumental means, who have felt their own wants and supplied them in their own way." The qualities which enabled Mr. Lassell to do all this made him what he

<sup>1</sup> Based on an obituary notice written by the present writer for the *Times*.